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Physics Procedia 55 (2014) 403 – 408

Physics Procedia

8th International Conference on Material Sciences, CSM8-ISM5

# Enhanced photocatalytic degradation of salicylic acid in water-ethanol mixtures from titanium dioxide grafted with hexadecyltrichlorosilane

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**Abstract**

The aim of this paper is to study the effect of the chemical modification on the photocatalytic properties of $TiO_2$. The $TiO_2$ Degussa-P25 nanoparticles are chemically modified using the hydrophobic organosilane hexadecyltrichlorosilane (HTS). The samples are employed as catalysts for salicylic acid photocatalytic oxidation in water-ethanol mixtures. The kinetics of salicylic acid photodegradation is investigated as a function of ethanol content in water-ethanol mixtures and initial HTS concentrations. The results indicate that the HTS groups are not degraded during the photocatalytic process. The $TiO_2$ grafted by HTS is more efficient than bare $TiO_2$ for the photodegradation process in presence of ethanol. The photodegradation process follows first order kinetics and the apparent rate constant increases linearly with the initial HTS concentration (amount of HTS grafted).

*Key words: Photocatalysis, $TiO_2$, HTS, ethanol, salicylic acid*



Peer-review under responsibility of the Organizing Committee of CSM8-ISM5

*Keywords:*

## 1. Introduction

Photocatalysis is a potential technology for the destruction of organic contaminants in water, such as aromatic compounds, which present a potential hazard to the environment. The mineralization of

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Peer-review under responsibility of the Organizing Committee of CSM8-ISM5
doi:10.1016/j.phpro.2014.07.058

remaining traces of organic contaminants in water together with the removal of microorganisms make photocatalysis a very suitable technique for the treatment of wastewater. Titanium dioxide ($TiO_2$) is the most commonly-used semiconductor photocatalyst since it is highly photoactive, photostable, biologically and chemically inert, and relatively inexpensive. The bandgap energy of $TiO_2$ is about 3 eV. Thus, when $TiO_2$ is illuminated by UV, it produces electron-hole pairs on the surface. The charge carriers created can, if they do not recombine, be trapped by titanium or surface hydroxyl groups. In the presence of oxygen and water, the trapped carriers then form free radicals that are highly oxidizing species that could mineralize organic pollutants.

However, the presence of ethanol in the aqueous solution induces a detrimental effect to the photocatalytic degradation of several pollutants [1,2]. To our knowledge no successful approach has been proposed to solve this problem. Over the last decades, increasing attention has been focused on the modification of the $TiO_2$ surface with organosilane molecules. Research studies had reported that surface modification of $TiO_2$ nanoparticles with silane agents inhibits the photocatalytic activity of the nano-material in water in absence of ethanol [3,4]. The objective of this work is to enhance the photodegradation efficiency of $TiO_2$ in water/ethanol mixtures, polluted by salicylic acid, by modifying the surface of $TiO_2$ nanoparticles with hexadecyltrichlorosilane (HTS). The HTS chains have been chosen in order to increase hydrophobic character of the photocatalyst.

## 2. Materials and Methods

### 2.1 Photocatalysts preparation and characterization

$TiO_2$ P25 Degussa nanoparticles of BET ($N_2$) specific surface area equals to $59.3 \pm 1.5$ $m^2/g$ was used without additional purification. The surface of $TiO_2$ was chemically modified using the hydrophobic organosilane N-hexadecyltrichlorosilane (HTS) according to the procedure of Alloul et al. [5]. First, the powder was heated in an oven at 120 °C for 8 hours. At this stage, 1 g of $TiO_2$ was dispersed into 100 mL of absolute ethanol solution containing hexadecyltrichlorosilane (HTS) at different initial concentrations ranging from 0.1 mM to 4 mM. The mixtures were stirred for 18 hours at room temperature. After 18 hours, the reaction was stopped and the samples were centrifuged at 7000 RCF (g) during 8 min at 15 °C. Then, the particles were washed with ethanol, centrifuged two times and then dried at 120 °C for 10 hours.

The Fourier transform infrared spectroscopy (FTIR) was helpful to monitor the mechanism of the chemical modification of $TiO_2$ with HTS molecules. Diffuse reflectance spectra were recorded using a Fourier transform infrared spectrometer equipped with a large-band mercury cadmium telluride detector cooled at 77 K and associated with a diffuse reflectance attachment.

### 2.2 Photodegradation experiments

Using the expertise through our previous work, salicylic acid was chosen as a model organic compound to evaluate the photoactivity of the bare and modified $TiO_2$ [6,7]. Salicylic acid solutions were prepared in ethanol-water mixtures and aerated before use. We used a standard initial salicylic acid concentration of 10 mg $L^{-1}$, while the titania concentration was equal to 1 g $L^{-1}$.

Photocatalytic and adsorption experiments were performed at room temperature in a static batch photoreactor open to air. This reactor consisted of a tubular quartz tube with 80 mL capacity. A magnetic stirrer guaranteed an oxygenation from atmospheric air and a satisfactory mixing of the reaction mixture with the $TiO_2$ suspension. The irradiation was assured by artificial light using a mercury lamp emitting in the near-UV. The lamp and the reactor were inserted in an ellipsoidal based cylinder made of polished aluminum which allowed to reflect the maximum amount of light into the reactor. The lamp and the reactor were positioned along the two parallel focal axes of the elliptically based cylinder. The intensity of the UV-light reaching the middle of the solution was measured with an UV radiometer and indicated a spectral response centered at 336 nm while the mean value of the radiation power impinging on the reacting suspension was estimated to be $10^{-5}$ Einstein $L^{-1}$ $s^{-1}$.

In each experiment, prior to UV irradiation, the $TiO_2$ suspension containing salicylic acid was magnetically stirred in the dark for 1 hour until adsorption/desorption equilibrium was reached. This was sufficient to reach an equilibrated adsorption concentration [8]. The solution was then irradiated under UV light with continuous magnetic stirring to keep the suspension homogeneous. To determine the change of the salicylic acid concentration during UV irradiation, aliquots of 3 mL of the suspension were withdrawn at appropriate times from the reactor using a glass syringe. The withdraw liquid was separated from $TiO_2$ particles by filtration through Millipore membranes (0.2 μm pore size). A first sample was taken at the end of the dark adsorption period, just before the light was turned on, in order to determine the concentration of pollutant in solution (nonadsorbed). The photocatalytic degradation of salicylic acid was followed by measuring the absorbance value at $\lambda$ = 300 nm, using a UV-visible spectrophotometer, initially calibrated, according to Beer-Lambert's law.

## 3. Results and discussion

### *3.1 $TiO_2$/HTS characterization*

The FTIR is usually employed to monitor the immobilization process of a ligand on native surfaces. The Figure 1 shows the superposition of the FTIR diffuse spectra of bare and modified $TiO_2$. In the presence of HTS on the surface, the appearance of absorption peaks between 2800 and 3000 $cm^{-1}$, characteristic to the stretching of $CH_3$ and $CH_2$ groups, confirms the adsorption of HTS molecules on the surface of $TiO_2$. We previously demonstrated that the substitution reaction (grafting) can be summarized as [5]:

$$(CH_3)_{15}CH_2Si(Cl)_3 + n{=}Si{-}OH \rightarrow n{=}Si{-}O{-}SiCH_2(CH_3)_{15}Cl_{(3-n)} + n\,HCl \quad (1)$$

where n is the number of bonds between the HTS molecules and the surface hydroxyl groups.
The FTIR diffuse spectrum of modified $TiO_2$ at the end of the photocatalytic experiment is also displayed in Fig. 1. Surprisingly, the spectra of the modified $TiO_2$ before and after the photocatalytic reaction are identical. In addition, the absorption peaks between 2800 and 3000 $cm^{-1}$ remain on the surface during the reaction. This emphasizes that the HTS groups are not degraded during the photocatalytic process.

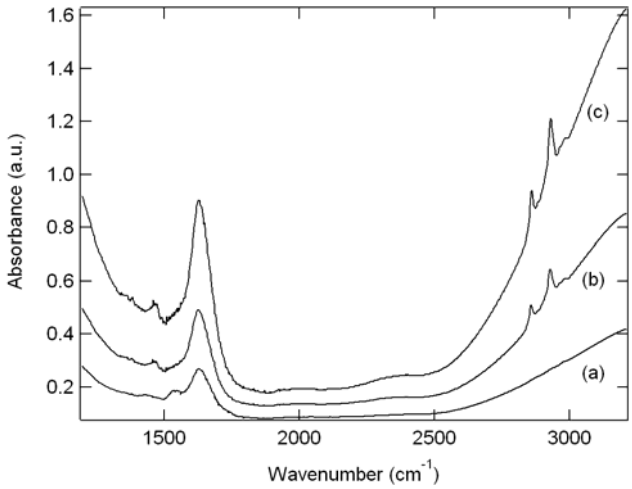


Fig. 1. FTIR diffuse spectra of (a) bare $TiO_2$, (b) modified $TiO_2$ before photocatalysis and (c) modified $TiO_2$ after photocatalytic experiments. The modified $TiO_2$ are prepared at 0.25 mM initial HTS concentration.

### 3.2 Photocatalytic results

#### *3.2.1 Influence of ethanol content*

The dependence of the amount of ethanol in the water/ethanol mixture on the time course of the photocatalytic degradation of salicylic acid using modified $TiO_2$ is illustrated in Fig. 2a. The modified

$TiO_2$ are prepared at 0.1 mM initial HTS concentration. Each curve shows the bulk concentration of salicylic acid as a function of the irradiation time. The salicylic acid concentration decreases with the irradiation time. The photocatalytic performances are significantly affected by the amount of ethanol. The maximum salicylic acid degradation is observed in pure water. In absence of ethanol, about 75% degradation of salicylic acid is observed at the end of 150 min. In the presence of ethanol, there is some salicylic acid degradation, but the efficiency of the degradation is inferior to that of pure water. In addition, the increase of the ethanol content produces a reduction of the photocatalytic activity. In pure ethanol, no degradation is observed over a long period and irradiation for 150 min produces no appreciable reduction in the salicylic acid concentration. So the reduction of the photocatalytic degradation is mainly due to the presence of ethanol.

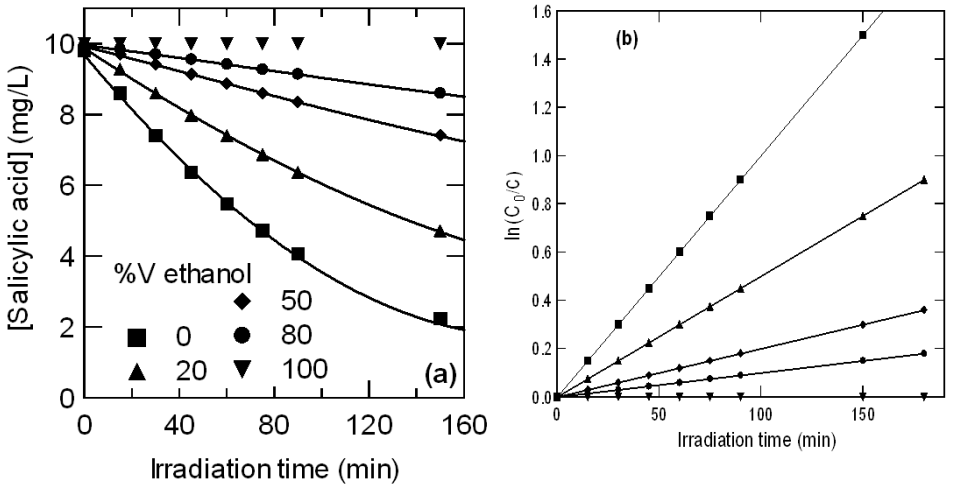


Fig. 2. (a) The effect of ethanol content on the photodegradation efficiency of salicylic acid using modified $TIO_2$/HTS at different irradiation times. The modified $TiO_2$ are prepared at 0.1 mM initial HTS concentration. (b) Kinetics of salicylic acid photodegradation. Linear transform $\ln(C_0/C)$ versus time t in photocatalytic experiments using modified $TiO_2$/HTS for different concentrations of ethanol.

The degradation experiments by UV irradiation of salicylic acid solutions containing $TiO_2$/HTS are expected to follow the pseudo-first-order kinetics with respect to the salicylic acid concentration in the bulk solution (C):

$$-\frac{dC}{dt} = k_{app} C \tag{2}$$

Integration of that equation, considering that $C = C_0$ at $t = 0$, with $C_0$ being the initial concentration in the bulk solution after dark adsorption and t the reaction time, leads to:

$$\ln\left(\frac{C_0}{C}\right) = k_{app} t \tag{3}$$

where $k_{app}$ stands for the apparent pseudo-first-order rate constant. A plot of $\ln(C_0/C)$ versus t for all the experiments performed with different ethanol concentrations is shown in Fig. 2b. The linear increase of $\ln(C_0/C)$ as a function of t is in perfect agreement with Eq. (3). This confirms that, at the low concentration of pollutant employed in the study, the photocatalytic degradation of salicylic acid obeys first order kinetics. The values of $k_{app}$ can be obtained directly from the regression analysis of the linear curve in the plot. In pure water, the rate constant equals 0.01 $min^{-1}$. The rate constant is reduced in the

presence of ethanol and it decreases to almost zero for pure ethanol. The decrease in the rate constant with the ethanol concentration was already observed for bare $TiO_2$ [1,2]. The diminution of $k_{app}$ reveals that the photoreaction is greatly inhibited by the presence of ethanol in solution. This behavior can be explained by the scavenger effect of ethanol which acts as a trap of free radicals generated by the photocatalytic reaction. Water and ethanol compete for the same adsorption sites on the surface of $TiO_2$ catalysts to react with the surface hydroxyl groups. Experimentally, this competition produces a decrease in the photocatalytic degradation of salicylic acid. The higher the ethanol concentration, the more ethanol molecules are preferred at the surface compared to water and salicylic acid.

### *3.2.2 Influence of HTS concentration*

The effect of the amount of HTS grafted onto the $TiO_2$ particles on the photodegradation efficiency of salicylic acid is examined. A 50-50 % v/v water/ethanol mixture is used. The results are shown in Fig. 3a. The photocatalytic performance is significantly affected by the initial HTS concentration. The photodegradation efficiency increases with the initial HTS concentration. For bare and modified $TiO_2$ prepared at 0.1 mM initial HTS concentration, there is some salicylic acid degradation, but the efficiency of the degradation is inferior to that of the higher HTS concentrations. The salicylic acid concentration decreases weakly with the irradiation time and the degradation of about 20% of salicylic acid is reported at the end of 150 min. When the initial HTS concentration equal 4 mM the degradation of the pollutant increases to 75%. As previously observed, the photocatalytic degradation of salicylic follows first order kinetic regardless of the HTS concentration (not shown). The trend is quite straightforward in view of the HTS adsorption behavior. The adsorption of the HTS onto the $TiO_2$ particles is expected to increase with the HTS concentration. It was previously observed that the HTS adsorbed amount increases with the initial HTS concentration up to a plateau that can be observed for an initial HTS concentration of 3 mM [5]. This illustrates that the variation of the photocatalytic performance reflects the change in the HTS adsorbed amount. The enhancement of the photocatalytic activity with the HTS initial concentration may have two origins: (i) increase of particle stability and/or (ii) hydrophobic effect.

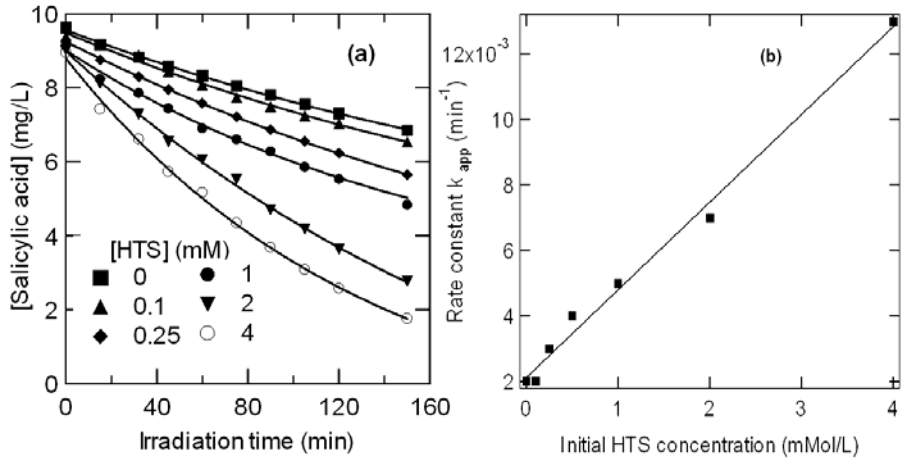


Fig. 3. (a) The effect of the initial HTS concentration on the photodegradation efficiency of salicylic acid using modified $TIO_2$/HTS at different irradiation times. A 50-50 % v/v water/ethanol mixture is used. (b) Influence of the initial HTS concentration on the apparent pseudo-first-order rate constant $k_{app}$ during the photodegradation of salicylic acid using modified $TIO_2$/HTS.

We believe that both effect occurs (i and ii). It is then relevant to determine if the increase in the photocatalytic performance is due to a hydrophobic effect. Considering that very roughly the HTS

adsorbed amount increases linearly with the HTS initial concentration, the increase of the initial HTS concentration converges logically to an increase of the photocatalytic activity. In the frame of this report we limit the discussion to the basic trends of the initial HTS concentration. We are aware however that the photocatalytic activity is more likely governed by the actual HTS adsorbed amount rather than the initial HTS concentration. Therefore, the Fig. 3b displays the evolution of the apparent pseudo-first-order rate constant $k_{app}$ as a function of the initial HTS concentration. The data points fall on a single line indicating that $k_{app}$ increases linearly with the initial HTS concentration, which is expected theoretically if the HTS adsorbed amount determines the photocatalytic activity. The photocatalytic activity is directly connected to an increase of the HTS adsorbed amount. Changes noted in Fig. 3a can be explained by the following: when the concentration of HTS increases the salicylic acid molecules rearrange all along the chain by hydrophobicity effect. Thus the free radicals generated by the photocatalytic reaction have positive probability of attack.

## 4. Conclusion

The aim of this paper was to study the effect of the chemical modification on the photocatalytic activity of $TiO_2$ particles. Our observations demonstrate that the hydrophobic organosilane hexadecyltrichlorosilane (HTS) molecules are grafted to the surface via reaction with hydroxyl groups. The photocatalytic activity of the modified titania samples has been tested on the photodegradation of salicylic acid in water-ethanol mixtures. The degradation is investigated as a function of ethanol content in water-ethanol mixtures and initial HTS concentrations. The results indicate that the HTS groups are not degraded during the photocatalytic process. The efficiency of the process depends on the HTS adsorbed amount and ethanol content. The surface-modified $TiO_2$ enhances the photocatalytic degradation efficiency of salicylic acid in water-ethanol mixtures. The photodegradation process follows first order kinetics and the apparent rate constant increases linearly with the initial HTS concentration (amount of HTS grafted).

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